

Hydrido Ru^{II} organometallics; synthesis, spectral and catalytic hydrogenation studies

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Abstract : The reaction between RuCl₂·3H₂O and tertiary phosphines in formaldehyde results in the formation of hydrido organometallics of the type [RuH(Cl)(CO)L₃]. From these another series of hydrido organometallics were derived by replacing one of the tertiary phosphines with pyrazole moiety and isolated the compounds of type [RuH(Cl)(CO)L₂Pz], where L = (2-formylphenyl)diphenylphosphine, (3-carboxyphenyl)diphenylphosphine, bis(3-carboxyphenyl)phenylphosphine, tris(3-carboxyphenyl)phosphine, (4-carboxyphenyl)diphenylphosphine, bis(4-carboxyphenyl)phenylphosphine, tris(4-carboxyphenyl)phosphine, (2-pyridyl)diphenylphosphine.

Keywords : Hydrido compounds, organometallics, catalytic hydrogenation, ruthenium(II).

The field of organometallic chemistry of transition metals is developing very fast because of its variety of applications and importance in the area of coordination chemistry^{1,2}. In the past attention has been paid on the design and the synthesis of organometallics but the importance of organometallic compounds is now well recognized^{3,4}. The ruthenium organometallics involving phosphorous donor ligands has excited great interest among chemists in recent years, due to the applications of these compounds in catalysis^{5,6}. Ruthenium hydrido compounds, by virtue of their wide range of reversible and accessible oxidation states, have proved to be useful catalysts in many reactions, such as hydrogenation, oxidation, carbonylation, hydroformylation etc.⁷⁻¹⁰. The desire to find highly water soluble and air stable organometallic complexes had led us to investigate organometallics of platinum group metals involving substituted tertiary phosphine ligands¹¹⁻¹⁴. The present investigation involves the synthesis, spectral and catalytic hydrogenation of hydrido Ru^{II} organometallics containing carboxyl/formyl/pyridyl substituted tertiary phosphines.

Results and discussion

The molecular formulae proposed for all the organometallics are based on the assumption that the ruthenium combines with phosphine ligands in 1 : 3 molar ratio for 1-8 and 1 : 2 for 9-16 organometallics. It is clear from the analytical data that the experimental values are in good agreement with the calculated ones (Table 1).

The organometallics (1-8) exhibit a weak band corresponding to $\nu(\text{Ru-H})$ in the range of 1980–2000 cm⁻¹

where as the organometallics 9-16 possess a strong band around 2040 cm⁻¹. This change in the absorption of $\nu(\text{Ru-H})$ can be assigned to pyrazole involvement with metal centre in *trans* position¹⁵. All the Ru^{II} organometallics (1-16) showed a strong peak in the range of 1903–1980 cm⁻¹ and these values are assigned to the $\nu(\text{CO})$ which coordinated to Ru^{II} metal centre. The absorption peak shown by all complexes (9-16) in the range 1500–1600 cm⁻¹ corresponding to $\nu(\text{C=C}) + \nu(\text{C=N})$ is attributed to the involvement of pyrazole nitrogen in the coordination¹⁵. The IR spectra of complexes 2-7, 10-15 exhibit a strong characteristic absorption band in the range 1705–1720 cm⁻¹ for $\nu(\text{COOH})$ which indicates the non-participation of this group in coordination¹⁶⁻¹⁸. The absorption band exhibited by the complexes 1, 9 in the range of 1680–1690 cm⁻¹ corresponding to $\nu(\text{CHO})$ is attributed to uncoordinated formyl functional group of tertiary phosphine to the metal centre¹⁹. Complexes 8 and 16 show an absorption peak in the range 1560–1580 cm⁻¹ is attributed to uncoordinated pyridyl nitrogen of (2-pyridyl)-diphenylphosphine ligand²⁰. The phosphine coordination $\nu(\text{Ru-P})$ is identified by observing a new strong absorption band in all complexes in the far IR region in the range of 509–520 cm⁻¹²¹. The far IR spectra of all complexes have shown one absorption band in the range of 309–314 cm⁻¹ which is assigned to $\nu(\text{Ru-Cl})$ ¹.

The ¹H NMR spectra of hydrido complexes 1-16 show a signal in the range –13.45 to –8.30 ppm due to the Ru–H proton²². The ¹H NMR spectra of complexes 2-7, 10-15 exhibit one sharp signal in the downfield around 11.80–12.80 ppm is assigned to uncoordinated carboxylic functional group

Table 1. Physical and analytical data of Ru^{II} organometallics with tertiary phosphines

Complex no.	Ru ^{II} complex formed	Decomp. temp. (°C)	Color	Yield (g, %)	Analyses (%): Found/(Calcd.)		
					C	H	N
1	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₆ H ₄ CHO) ₃]	217	White	0.347 (71%)	66.74 (67.18)	3.94 (4.43)	-
	C ₅₈ H ₄₆ O ₄ P ₃ Cl ₂ Ru						
2	[RuH(Cl)(CO)(Ph ₂ -P-3-C ₆ H ₄ COOH) ₃]	220	White	0.402 (80%)	63.82 (64.21)	4.12 (4.15)	-
	C ₅₈ H ₄₆ O ₇ P ₃ ClRu						
3	[RuH(Cl)(CO)(Ph ₂ -P-(3-C ₆ H ₄ COOH) ₂) ₃]	225	Cream	0.512 (72%)	60.40 (60.24)	3.90 (3.78)	-
	C ₆₁ H ₄₆ O ₁₃ P ₃ ClRu						
4	[RuH(Cl)(CO)(P-(3-C ₆ H ₄ COOH) ₃) ₃]	235	Light yellow	0.543 (70%)	56.90 (57.01)	3.60 (3.41)	-
	C ₆₄ H ₄₆ O ₁₉ P ₃ ClRu						
5	[RuH(Cl)(CO)(Ph ₂ -P-4-C ₆ H ₄ COOH) ₃]	225	White	0.402 (82%)	63.27 (64.20)	4.02 (4.15)	-
	C ₅₈ H ₄₆ O ₇ P ₃ ClRu						
6	[RuH(Cl)(CO)(Ph-P-(4-C ₆ H ₄ COOH) ₂) ₃]	232	Light cream	0.501 (70%)	60.35 (60.24)	3.86 (3.78)	-
	C ₆₁ H ₄₆ O ₁₃ P ₃ ClRu						
7	[RuH(Cl)(CO)(P-(4-C ₆ H ₄ COOH) ₃) ₃]	240	White	0.551 (71%)	56.97 (57.01)	3.65 (3.41)	-
	C ₆₄ H ₄₆ O ₁₉ P ₃ ClRu						
8	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₅ H ₄ N) ₃]	238	Light cream	0.405 (85%)	65.11 (65.34)	4.23 (4.53)	2.52 (2.93)
	C ₅₂ H ₄₃ N ₃ P ₃ ClRu						
9	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₆ H ₄ CHO) ₂ (Pz)]	245	Light cream	0.297 (73%)	60.99 (61.84)	4.02 (4.30)	-
	C ₄₂ H ₃₅ O ₃ P ₂ ClN ₂ Ru						
10	[RuH(Cl)(CO)(Ph ₂ -P-3-C ₆ H ₄ COOH) ₂ (Pz)]	228	Light cream	0.310 (75%)	59.12 (60.15)	4.01 (4.86)	3.02 (3.20)
	C ₄₄ H ₃₉ O ₅ P ₂ N ₂ ClRu						
11	[RuH(Cl)(CO)(Ph-P-(3-C ₆ H ₄ COOH) ₂)(Pz)]	241	Light yellow	0.312 (74%)	57.60 (57.41)	3.96 (4.06)	3.02 (2.91)
	C ₄₆ H ₃₉ O ₉ P ₂ N ₂ ClRu						
12	[RuH(Cl)(CO)(P-(3-C ₆ H ₄ COOH) ₃)(Pz)]	253	Cream	0.326 (74%)	55.00 (54.88)	3.60 (3.71)	2.70 (2.66)
	C ₄₈ H ₃₉ O ₁₃ P ₂ N ₂ ClRu						
13	[RuH(Cl)(CO)(Ph ₂ -P-4-C ₆ H ₄ COOH) ₂ (Pz)]	226	White	0.308 (73%)	58.15 (60.15)	4.13 (4.46)	3.21 (3.20)
	C ₄₄ H ₃₉ O ₅ P ₂ N ₂ ClRu						
14	[RuH(Cl)(CO)(Ph-P-(4-C ₆ H ₄ COOH) ₂)(Pz)]	234	Cream	0.311 (72%)	57.54 (57.41)	4.08 (4.06)	2.86 (2.91)
	C ₄₆ H ₃₉ O ₉ P ₂ N ₂ ClRu						
15	[RuH(Cl)(CO)(P-(4-C ₆ H ₄ COOH) ₃)(Pz)]	247	Light grey	0.336 (76%)	55.02 (54.88)	3.82 (3.71)	2.51 (2.66)
	C ₄₈ H ₃₉ O ₁₃ P ₂ N ₂ ClRu						
16	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₅ H ₄ N) ₂ (Pz)]	212	Light cream	0.272 (70%)	59.43 (60.20)	3.97 (4.69)	6.91 (7.10)
	C ₄₀ H ₃₇ ON ₄ P ₂ ClRu						

of tertiary phosphine¹⁶⁻¹⁸. The absorbance peak which is exhibited by the complexes 1 and 9 around 10.60 ppm reveals that the non involvement of formyl group of tertiary phosphine in the coordination¹⁷⁻¹⁹. The triplet signal exhibited by the complexes 9-16 in the range 6.02-6.31 ppm is attributed to 4H of pyrazole confirms the involvement of pyrazole in the coordination with metal centre²³. The multiplet signals which appeared in all the complexes in the range 6.40-8.50 ppm are attributed to aromatic protons. The ¹H NMR spectral data of Ru^{II} organometallics is presented in the Table 2.

¹³C NMR signals for the present series of Ru^{II} complexes are assigned by the comparison with the spectra of corresponding free ligands. An inspection of the chemical shift in ¹³C NMR spectra of these complexes reveals a consistent

pattern. In all the complexes, the resonance of carbon atom which involved in coordination to the Ru^{II} metal is shifted ~20-30 ppm. The signal exhibited by all complexes around 126-140 ppm is attributed to aromatic carbons of tertiary phosphines. The sharp peak found in the spectra of complexes 9-16 in the range of 141-143 ppm is assigned to carbons of pyrazole²³. The presence of carbonyl carbon signal in the range of 210-217 ppm for the complexes 1-16 suggests its coordination with ruthenium metal²⁴. The signal exhibited by complexes 1, 9 at 184 ppm is attributed to the uncoordinated formyl group of tertiary phosphine²⁵. The sharp signal exhibited by the complexes 2-7, 10-15 in the range of 172-176 ppm is attributed to the non-involvement of carboxylic functional group of tertiary phosphine¹⁶⁻¹⁸.

Table 2. ¹H NMR spectral data of Ru^{II} organometallics

Sl. no.	Compd.	Ru-H (t)	¹ H peak position (ppm)		
			Pyrazole 4H (t)	Tertiary phosphines	
				Aryl (m)	COOH (br)
1	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₆ H ₄ CHO) ₃]	-10.58	-	6.73-8.30	10.65 ^a
2	[RuH(Cl)(CO)(Ph ₂ -P-3-C ₆ H ₄ COOH) ₃]	-13.41	-	6.80-8.50	11.35
3	[RuH(Cl)(CO)(Ph-P-(3-C ₆ H ₄ COOH) ₂) ₃]	-12.02	-	6.75-8.10	11.40
4	[RuH(Cl)(CO)(P-(3-C ₆ H ₄ COOH) ₃) ₃]	-13.21	-	6.95-8.20	12.25
5	[RuH(Cl)(CO)(Ph ₂ -P-4-C ₆ H ₄ COOH) ₃]	-12.04	-	6.75-8.10	12.78
6	[RuH(Cl)(CO)(Ph-P-(4-C ₆ H ₄ COOH) ₂) ₃]	-12.84	-	7.00-8.01	11.60
7	[RuH(Cl)(CO)(P-(4-C ₆ H ₄ COOH) ₃) ₃]	-13.00	-	7.02-8.25	12.13
8	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₅ H ₄ N) ₃]	-13.01	-	6.70-8.20	-
9	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₆ H ₄ CHO) ₂ (Pz)]	-10.52	6.02	6.50-7.80	10.56 ^a
10	[RuH(Cl)(CO)(Ph ₂ -P-3-C ₆ H ₄ COOH) ₂ (Pz)]	-8.30	6.02	6.40-7.80	12.40
11	[RuH(Cl)(CO)(Ph-P-(3-C ₆ H ₄ COOH) ₂) ₂ (Pz)]	-9.24	6.15	6.50-7.84	12.80
12	[RuH(Cl)(CO)(P-(3-C ₆ H ₄ COOH) ₃) ₂ (Pz)]	-10.52	6.05	6.60-7.65	12.48
13	[RuH(Cl)(CO)(Ph ₂ -P-4-C ₆ H ₄ COOH) ₂ (Pz)]	-12.04	6.13	6.80-7.20	12.50
14	[RuH(Cl)(CO)(Ph-P-(4-C ₆ H ₄ COOH) ₂) ₂ (Pz)]	-11.45	6.20	6.56-7.90	12.74
15	[RuH(Cl)(CO)(P-(4-C ₆ H ₄ COOH) ₃) ₂ (Pz)]	-10.25	6.25	6.65-7.85	13.01
16	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₅ H ₄ N) ₂ (Pz)]	-10.04	6.31	6.54-7.50	-

^a -CHO.

³¹P NMR spectra of organometallics 1-8 exhibit a doublet signal in the range 22.01-26.50 ppm for the presence of two mutually *trans* phosphorous nuclei of tertiary phosphine ligands. The appearance of the another triplet signal in the range 30.90-39.62 ppm is assigned to the third phosphorous nucleus of tertiary phosphine ligand. This reveals that phosphines are arranged in an octahedral geometry with mer-

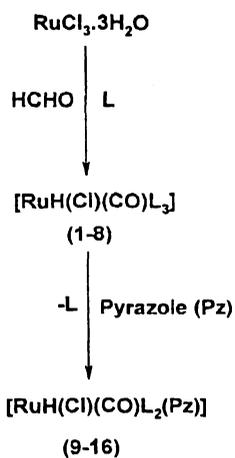
trans or mer-*cis* configuration²⁶. Further, the complexes 9-16 which exhibit only one singlet peak in the range of 38.26-44.02 ppm reveals that the two phosphorous atoms of tertiary phosphine ligands are arranged *trans* to each other²⁷.

The ¹³C and ³¹P NMR spectral data of ruthenium(II) organometallics is given in the Table 3.

Table 3. ¹³C NMR, ³¹P NMR spectral data of Ru^{II} organometallics

Sl. no.	Compd.	CO	¹³ C peak positions (ppm)			³¹ P peak position (ppm)
			Pyrazole C=C	C=N	Tertiary phosphines Aryl (m) COOH (br)	
1	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₆ H ₄ CHO) ₃]	217.00	-	-	126-134 185 ^a	39.60 (t), 25.36 (d)
2	[RuH(Cl)(CO)(Ph ₂ -P-3-C ₆ H ₄ COOH) ₃]	213.34	-	-	129-136 173	32.63 (t), 22.08 (d)
3	[RuH(Cl)(CO)(Ph-P-(3-C ₆ H ₄ COOH) ₂) ₃]	212.24	-	-	128-138 175	30.90 (t), 24.12 (d)
4	[RuH(Cl)(CO)(P-(3-C ₆ H ₄ COOH) ₃) ₃]	214.31	-	-	127-139 176	33.12 (t), 22.01 (d)
5	[RuH(Cl)(CO)(Ph ₂ -P-4-C ₆ H ₄ COOH) ₃]	215.27	-	-	130-138 174	34.35 (t), 23.02 (d)
6	[RuH(Cl)(CO)(Ph-P-(4-C ₆ H ₄ COOH) ₂) ₃]	215.14	-	-	129-136 173	36.75 (t), 24.65 (d)
7	[RuH(Cl)(CO)(P-(4-C ₆ H ₄ COOH) ₃) ₃]	212.90	-	-	130-140 175	38.45 (t), 25.03 (d)
8	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₅ H ₄ N) ₃]	216.43	-	-	128-140 -	34.02 (t), 25.05 (d)
9	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₆ H ₄ CHO) ₂ (Pz)]	210.02	104.13	141.00	126-134 183 ^a	39.62
10	[RuH(Cl)(CO)(Ph ₂ -P-3-C ₆ H ₄ COOH) ₂ (Pz)]	214.12	104.13	140.10	126-136 176	43.53
11	[RuH(Cl)(CO)(Ph-P-(3-C ₆ H ₄ COOH) ₂) ₂ (Pz)]	213.97	103.54	142.56	128-136 174	37.56
12	[RuH(Cl)(CO)(P-(3-C ₆ H ₄ COOH) ₃) ₂ (Pz)]	214.46	102.12	141.87	126-134 175	44.02
13	[RuH(Cl)(CO)(Ph ₂ -P-4-C ₆ H ₄ COOH) ₂ (Pz)]	215.32	102.12	143.00	134-137 172	38.26
14	[RuH(Cl)(CO)(Ph-P-(4-C ₆ H ₄ COOH) ₂) ₂ (Pz)]	211.46	104.50	142.45	127-138 172	41.25
15	[RuH(Cl)(CO)(P-(4-C ₆ H ₄ COOH) ₃) ₂ (Pz)]	213.84	102.98	141.95	126-140 176	39.52
16	[RuH(Cl)(CO)(Ph ₂ -P-2-C ₅ H ₄ N) ₂ (Pz)]	215.22	103.12	142.13	126-138 -	38.65

^a -CHO, ^b -CH₂-COOH.



where, L = Ph₂P-2-C₆H₄CHO, Ph₂P-3-C₆H₄COOH, PhP-(3-C₆H₄COOH)₂, P-(3-C₆H₄COOH)₃, Ph₂P-4-C₆H₄COOH, PhP-(4-C₆H₄COOH)₂, P-(4-C₆H₄COOH)₃, Ph₂P-2-C₃H₄N

Scheme 1. Synthetic route of the twelve Ru^{II} organometallics.

Table 4. Catalytic hydrogenation of Ru^{II} phosphine compounds and % yields of reduced products at 1.5 atm pressure of H₂ and 25 °C in DMF

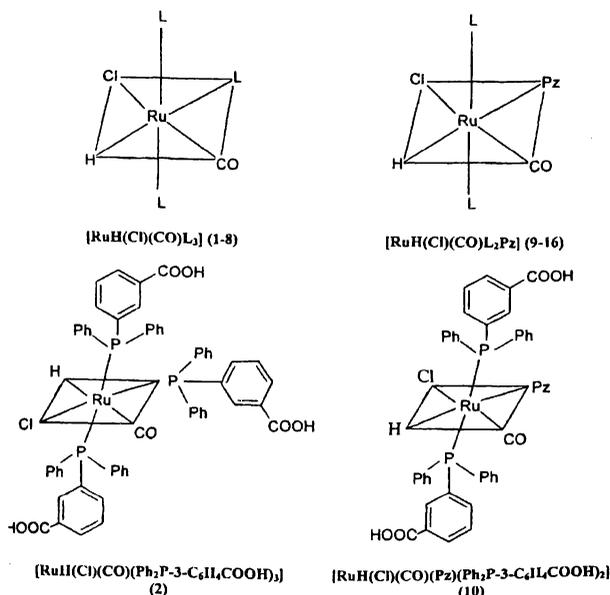
Substrate	Catalyst (mol/lit × 10 ⁻⁴)	Products	Yield (%)	
			1	9
Nitrobenzene	1, 9	Aniline	90	98
<i>o</i> -Nitrotoluene	1, 9	<i>o</i> -Toluidine	84	95
<i>o</i> -Chloronitrobenzene	1, 9	<i>o</i> -Chloroaniline	80	92
<i>p</i> -Nitrotoluene	1, 9	<i>p</i> -Toluidine	89	96
<i>m</i> -Dinitrobenzene	1, 9	<i>m</i> -Phenylenediamine	75	80
<i>m</i> -Chloronitrobenzene	1, 9	<i>m</i> -Chloroaniline	72	96
Styrene	1, 9	Ethyl benzene	82	95
Hex-1-ene	1, 9	Hexane	62	70
Hex-2-ene	1, 9	Hexane	30	32
Maleic acid	1, 9	Succinic acid	91	96
Isoprene	1, 9	2-Methylbutane	84	94
Cycloocta-1,5-diene	1, 9	Cyclooctane	88	94
Phenyl acetylene	1, 9	Ethyl benzene	90	98
Diphenyl acetylene	1, 9	1,2-Diphenyl ethane	87	98
Benzaldehyde	1, 9	Benzyl alcohol	92	97

The electronic spectra of the Ru^{II} organometallics were recorded in distilled CDCl₃. The electronic spectra of all the ruthenium(II) organometallics exhibit four absorption bands in the range of 650–243 nm due to ¹A_{1g} → ³T_{1g}, ³T_{2g}, ¹T_{1g} and ¹T_{2g} transitions. The bands appearing 351–309, 258–243 nm are due to charge transfer transitions²⁷. The electronic spectra of these organometallics indicate octahedral geometry around the Ru^{II} ion.

On the basis of analytical and spectral data octahedral structures have been tentatively proposed for all the Ru^{II} organometallics (Schemes 1 and 2).

Catalytic hydrogenations :

New ruthenium(II) complexes reduced the unsubstituted



Scheme 2. Proposed structures of twelve hydrido Ru^{II} organometallics.

or *p*-substituted nitro aromatics at much faster rates than the corresponding *o*-substituted compounds. Nitrobenzene is preferentially reduced almost to 95–99%, when admitted with any *ortho* substituted derivatives such as *o*-nitrotoluene and *o*-chloronitrobenzene. The catalytic hydrogenation of nitro aromatics leads to the formation of the corresponding amines in almost all cases except *m*-dinitrobenzene, where the final product was only the corresponding hydroxylamine²⁸. Alkenes underwent simultaneous reduction and isomerization to produce alkanes and alk-2-ens. The rates of reduction hex-1-ene and hept-1-ene were extremely slow. Styrene, isopropene or cycloocta-1,5-diene, in which the >C=C< group is a part of the delocalized system were reduced more rapidly than the isolated double bonds in cycloocta-1,5-diene. On hydrogenation of phenylethylene and phenylacetylene with the corresponding complexes resulted only ethylbenzene. It is observed that in case of phenylethylene the rate of hydrogenation reaction is very high than the rate of phenylacetylene, which may be due to the free rotation of π -electrons in the former one. Diphenylacetylene was reduced first to *cis*-stilbene and then to 1,2-diphenylethane. Diphenylacetylene was reduced at a faster rate than *cis*-stilbene and this may be due to superior coordinating capacity of the former to the metal centre²⁹. Catalyst 9 appears to be efficient as compared to catalyst 1 on the reduction of various substrates (Table 4). The catalytic activity of studied complexes may be arranged in the order of 9 > 1. The efficiency of a catalyst 9 is high due to the presence of pyrazole *trans* to the hydride having greater metal-ligand π -electron delocalization in the complex³⁰ and in turn which could easily labilize hydride ion in catalytic

reactions. Formation of very good yield of products under very mild reaction conditions suggests that these complexes can function as good catalysis on various substrates.

Experimental

All the solvents used in the present investigation are of analytical grade and were used without further purification. For the spectroscopic measurements organic solvents were purified according to the literature methods. The starting materials viz. RuCl₃·3H₂O, HCHO, pyrazole were obtained from Aldrich Chemical Company, Inc, F.R.G. All the substituted tertiary phosphines were prepared as per the literature methods¹⁶⁻¹⁸.

Elemental data was obtained by using a Perkin-Elmer 240C CHN elemental analyzer. Electronic spectra were recorded on a Shimadzu MPS-5000 spectrophotometer, IR spectra in KBr pellets on Nicolet 740 spectrophotometer, ¹H NMR spectra on Bruker WH 270 (270 MHz) using CDCl₃/DMSO solvent, ¹³C NMR on Bruker WH 270 (67.93 MHz), ³¹P NMR on WH 270 (109.29 MHz). The hydrogenation unit consists of three necked double walled glass drain which in turn is connected to a double walled hydrogen burette through which water at the desired temperature from a thermostat is circulated.

Synthesis of Ru^{II} organometallics of the type [RuH(Cl)(CO)L₃](OMC. 1-8) :

RuCl₃·xH₂O (0.5 mmol) dissolved in 2-methoxyethanol and aqueous formaldehyde (20 ml) was added to the solution of substituted tertiary phosphines (L) (1.5 mmol) dissolved in 2-methoxyethanol. The mixture was heated under reflux for 15 min and allowed to cool. The white precipitate formed was separated, washed with ethanol and water and dried *in vacuo*. The compound was recrystallised using dichloromethane and ethanol solvent mixture.

Synthesis of Ru^{II} organometallics of the type [RuH(Cl)(CO)L₂Pz](OMC. 9-16) :

The solution of [RuH(Cl)(CO)L₃] (0.25 mmol) dissolved in 12 ml of ethanol and was mixed with pyrazole (0.25 mmol) and the resultant mixture was subjected to reflux under heating for 25 min to get a cream coloured precipitate. The product was separated, washed with ethanol and dried *in vacuo*. The product was recrystallised using dichloromethane and ethanol solvent mixture.

Catalytic hydrogenation :

Dimethylformamide solution was saturated with hydrogen gas and then 0.01 mmol of catalyst was added. The catalyst goes in to the solution in few min. The reaction system was flushed with hydrogen for few min and a 0.01 mmol of substrate in DMF was injected. The hydrogen absorption

begins as soon as the shaking is started. The process was continued for 90 min. The resulting mixture was cooled and extracted with chloroform, the organic layer was separated, washed with water, dried over magnesium sulphate and evaporated to give the reduced product. The procedure is repeated by changing ruthenium catalyst.

Conclusions :

Based on the discussion of spectral data it is confirmed that the Ru^{II} metal centre is coordinated by hydride, carbonyl, chloride and three tertiary phosphine groups and also it reveals that phosphines are arranged in an octahedral geometry with *mer-trans* or *mer-cis* configuration. In the compounds 9-16 the two phosphines are arranged mutually *trans* to each other and a pyrazole in the place of one of the tertiary phosphine ligands. An octahedral structure is tentatively proposed for all the ruthenium(II) organometallics. Catalytic hydrogenation of some aromatic nitro compounds, alkenes, alkynes and aldehydes is carried out by using 1 and 9 compounds and their catalytic activity found to be in the order of 9 > 1 under mild conditions.

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